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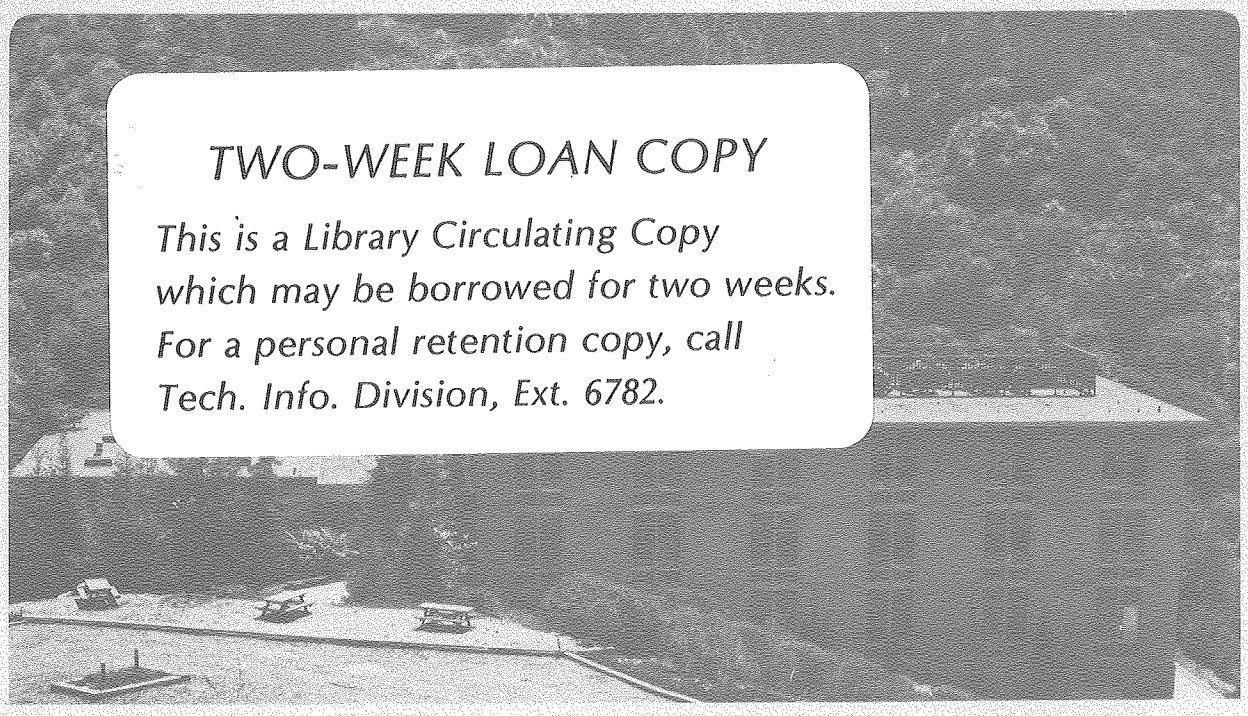

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PREPARATION AND STRUCTURAL CHARACTERIZATION OF α-NpF_5*

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Introduction

Until recently, only the pentafluorides of uranium and protactinium had been prepared, although thermodynamic calculations suggested NpF_5 and possibly PuF_5 should be stable (1). Russian workers (2) have recently reported the synthesis of NpF_5 by the oxidation of NpF_4 in anhydrous hydrogen fluoride with KrF_2 at room temperature. Analysis of this material by spectroscopic and analytical methods showed it to be NpF_5. We have recently developed a new and relatively simple synthesis for UF_5 (3) by the reaction of UF_6 dissolved in anhydrous hydrogen fluoride with excess PF_3. A similar reaction has now been carried out with NpF_6 with the resultant product being α-NpF_5.

Experimental

NpF_6 was dissolved in anhydrous hydrogen fluoride at room temperature in a Kel-F tube. This solution was frozen at 77K and an excess amount of PF_3 was condensed onto the frozen solution. The liquid N_2 bath was removed and the solution was allowed to warm to room temperature. A bluish-white ppt formed during the warming process. After warming to room temperature the anhydrous hydrogen fluoride, PF_3 and PF_5, were removed by distillation. Samples for x-ray analysis were prepared in an argon atmosphere box.

X-ray powder patterns were obtained with a 114 mm Debye-Scherrer camera using copper Kα radiation. All the lines in the powder pattern could be assigned on the basis of the α-UF_5 structure (4). The observed lines were fitted to the calculated pattern using the least squares program LCR-2 with the Nelson-Riley correction (5). The measured d-spacings, lattice parameters, and intensities are shown in Table 1.

TABLE 1

Powder Diffraction Data for α-NpF_5 at Room Temperature

Intensity[a]	hkl	Observed d spacings (Å)	Observed 2θ[b] (deg)	Calculated 2θ[b,c] (deg)
S+	110	4.611	19.25	19.26
S	101	3.678	24.20	24.23
M+	200	3.258	27.37	27.35
M+	211	2.440	36.83	36.84
M	220	2.308	39.03	39.04
W	002	2.222	40.60	40.54
S-	310	2.062	43.90	43.87
W+	112	2.004	45.24	45.24
M-	301	1.955	46.45	46.46
W+	202	1.840	49.55	49.58
W	321	1.676	54.77	54.74
W	400	1.633	56.35	56.38
W	222	1.604	57.47	57.53
W+	330	1.537	60.19	60.14
M-	312	1.514	61.22	61.24
M-	411	1.492	62.22	62.23
M-	420	1.459	63.77	63.77

[a] S = strong, M = medium, W = weak.

[b] Cu radiation - λ = 1.5418 Å.

[c] Tetragonal lattice a = 6.53 ± 0.03 Å, b = 4.45 ± 0.03 Å.

Results

Although the reaction utilized for the synthesis of NpF_5 was a low temperature one, the structure of α-NpF_5 determined is the same as α-UF_5, the high temperature form. The α-NpF_5 structure is consistent with the infrared and Raman spectra reported by the Russian workers (2).

The same reaction was run with PuF_6 but the product obtained was amorphous and had the same tan color as PuF_4.

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